**United States Environmental Protection Agency** **Office of Research and Development**

# National Exposure Research Laboratory
# FY02 Research Abstract

Government Performance Results Act (GPRA) Goal 2
APM 65

Significant Research Findings:

# Nationwide Disinfection By-Product Occurrence Study

**Scientific Problem and Policy Issues**

The Safe Drinking Water Act and Amendments requires that the U.S. Environmental Protection Agency (EPA) address disinfection by-products (DBPs) in drinking water. DBPs are formed when a disinfectant (such as chlorine, ozone, chlorine dioxide, or chloramine) reacts with organic matter and/or bromide naturally present in source waters (such as rivers, lakes, or groundwater). DBPs are of concern because epidemiologic studies indicate that some may be responsible for cancer and reproductive/developmental effects in human populations, and other studies have shown that high doses of certain DBPs cause cancer and other adverse health effects in laboratory animals. As a result, EPA has regulated several DBPs that occur most frequently and at the highest levels that may be responsible for adverse health effects. However, several hundred DBPs have been identified and reported in the literature, but only a very few of these have been studied for adverse health effects. Because health effects studies are extremely expensive, it is not possible to simply test all DBPs that are reported. Also, it is not wise to test DBPs for which there is no quantitative occurrence information (to know how widespread a particular DBP is and at what concentrations it is present). To obtain needed occurrence data, scientists from the National Exposure Research Laboratory (NERL) initiated a Nationwide DBP Occurrence Study in the United States to quantify high priority DBPs and to identify any new ones that have not been previously reported. Scientists from the University of North Carolina and the Metropolitan Water District of Southern California collaborated with NERL scientists on this effort. The top 50 DBPs resulting from a prioritization effort were included in this Nationwide Occurrence Study. These DBPs were selected by experts from the group of 500-600 DBPs that had been reported, according to predicted adverse health effects. Drinking water samples were collected across the United States from plants that use chlorine, ozone, chlorine dioxide, and/or chloramine for disinfection. Because DBPs may change in concentration or change in form (e.g., hydrolyze to form other chemicals), their fate and transport were also studied throughout the distribution system. The goals of this project were to determine the concentrations at which these DBPs occur, under what conditions they occur, how often they occur, whether they are

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| | hydrolyzed/transformed in the distribution system, and also to identify any new DBPs that have been overlooked previously. Results of this work will help to prioritize future health effects work on those DBPs that are found at the highest levels and at the most locations. |
| **Research Approach** | Drinking waters were chosen across the United States in locations to provide waters with low and high bromide, different pH conditions, and different organic matter levels. High bromide waters were included because naturally occurring bromide contributes to the formation of brominated DBPs, and certain brominated DBPs appear to be more toxic than similar chlorinated DBPs. These high bromide waters also contain significant levels of natural iodide, which contributes to the formation of iodinated DBPs, such as iodo-trihalomethanes, for which there is relatively little exposure and toxicity data. Regulated and Information Collection Rule DBPs were also measured for comparison purposes. Drinking water samples were collected both at the plant (following different stages of treatment) and in the distribution system. Chemical standards for most of the 50 high priority DBPs were synthesized (most could not be purchased commercially), and analytical methods were developed for quantifying them in drinking water. Quantitation methods involved various extraction and derivatization methods, along with gas chromatography (GC) or GC/mass spectrometry (MS) detection. For identifying new DBPs, advanced analytical techniques were used, including GC with low- and high-resolution electron ionization-MS and chemical ionization-MS. |
| **Results and Implications** | Most of the high priority DBPs were found in several drinking waters across the United States. High priority DBPs identified and quantified include 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and brominated forms of MX (the so-called BMXs), iodo-trihalomethanes, halomethanes, halonitromethanes, haloacids, haloacetonitriles, haloketones, haloacetates, haloamides, and a few non-halogenated DBPs. It was previously believed that MX would not be found at levels higher than 60 parts-per-trillion (ng/L); however, in this study, MX reached levels of 300-400 ng/L at certain locations. Iodinated DBPs, including iodo-trihalomethanes were also detected in most drinking waters sampled, even those with relatively low bromide/iodide levels. Because chloramines are used to reduce halomethane formation, it was surprising that iodo-trihalomethanes were highest at a plant that used chloramine for disinfection. Also surprising was that while ozone generally controls the formation of trihalomethanes and other trihalo species, some dihalo species (such as dihaloaldehydes) were higher at plants using pre-ozonation. Another unexpected finding was the discovery of iodo-acids. Iodo-acids have never been reported previously for any disinfectant. Five iodo-acids (iodoacetic acid, iodobromoacetic acid, iodobromopropenoic acid (2 isomers), and 2-iodo-3-methylbutenedioic acid) were identified in drinking water from a plant in the Southwest that used chloramine |

disinfection for high-bromide source waters. Many new brominated haloacids were also identified in drinking waters from several states. In addition to the high priority haloketones quantified in drinking water samples, other haloketones were also identified in selected samples. A number of these were analogous to the di-, tri-, and tetrahalogenated high priority haloketones, except that these were mixed bromochloro species. Likewise, dibromo- and bromodichloroacetaldehyde, brominated analogs of high priority haloacetaldehydes, were detected in selected samples. Brominated DBPs are important, as current toxicology (and some recent epidemiology) studies suggest that certain brominated DBPs may be of higher health concern than the chlorinated species. The use of broadscreen GC/MS methods provided complementary information to the survey for the high priority DBPs, which will allow for a better understanding of exposure to DBPs of potential health concern.

This research project directly supports ORD's research to ensure the safety of drinking water under the Government Performance and Results Act (GPRA) Goal 2 ("Clean and Safe Water"), Objective 1 ("Ensure Safe Drinking Water and Recreational Waters"), Sub-Objective 7 ("Conduct Safe Drinking Water Research"). The results of this project address GPRA annual performance goal (APG) 65 ("Report on the occurrence of chemical by-products from alternative drinking water systems"). This research expands our knowledge on the occurrence of DBPs beyond those that are currently regulated, will help to prioritize future DBP health effects research, and will allow EPA's Office of Water to make improved decisions regarding the safety of drinking water and to ultimately minimize any that are found to be hazardous.

**Research Collaboration and Publications**

This project was a large collaborative effort between scientists at NERL, scientists at the University of North Carolina (PI, Howard Weinberg), and the Metropolitan Water District of Southern California (PI, Stuart Krasner). The non-EPA scientists were responsible for designing the sampling strategy, developing analytical methods for the 50 high priority DBPs, and quantifying them in U.S. drinking waters. The EPA scientists were responsible for designing the project and identifying new, previously unknown DBPs. This research has been presented at several conferences and in the following proceedings manuscripts:

Krasner, S. W., Pastor, S., Chinn, R., Sclimenti, M. J., Weinberg, H. S., and Richardson, S. D. (2001). "The Occurrence of a New Generation of DBPs (Beyond the ICR)." *Proceedings of the Water Quality Technology Conference*, American Water Works Association.

Weinberg, H. S., Krasner, S. W., and Richardson, S. D. (2001). "Determination of New Carbonyl-Containing Disinfection By-products in Drinking Water." *Proceedings of the Water Quality Technology Conference*, American Water

Works Association.

Gonzalez, A. C., Krasner, S. W., Weinberg, H., and Richardson, S. D. (2000). "Determination of Newly Identified Disinfection By-products in Drinking Water." *Proceedings of the Water Quality Technology Conference*, American Water Works Association.

Onstad, G. D., Weinberg, H. S., Krasner, S. W., and Richardson, S. D. (2000). "Evolution of Analytical Methods for Halogenated Furanones in Drinking Water." *Proceedings of the Water Quality Technology Conference*, American Water Works Association.

Selected Presentations (in addition to American Water Works Association conferences):

Richardson, S. D., Thruston, A. D., Jr., Krasner, S. W., and Weinberg, H. S. "Results of a Nationwide DBP Occurrence Study: Identification of New DBPs of Potential Health Concern." International Society of Exposure Analysis (ISEA)-International Society for Environmental Epidemiology (ISEE) Conference. Vancouver, Canada. August, 2002.

Krasner, S., Chinn, R., Pastor, S., Sclimenti, M., Weinberg, H., Onstad, G., Richardson, S. D., and Thruston, A. D., Jr. "The Occurrence of Disinfection By-products of Health Concern in Drinking Water." International Society of Exposure Analysis (ISEA)-International Society for Environmental Epidemiology (ISEE) Conference. Vancouver, Canada. August, 2002.

A final report was completed: The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study; EPA/600/R-02/068. Several journal articles are also expected.

**Future Research**

As mentioned earlier, results of this project are expected to target future health effects research. In fact, scientists at EPA's National Health and Environmental Effects Laboratory and the University of Illinois have already begun to test some of the high priority DBPs (halonitromethanes) in initial toxicology screening assays. It is expected that health effects work will also begin on other DBPs that show significant occurrence in U.S. drinking waters.

**Contacts for Additional Information**

Questions and inquiries can be directed to:

Susan D. Richardson, Ph. D.
US EPA, Office of Research and Development
National Exposure Research Laboratory
960 College Station Rd.
Athens, GA 30605

Phone: 706/355-8304
E-mail: richardson.susan@epa.gov

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